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Asymmetric μ_2-1,1-azido bridged copper(II) complex: Synthesis, X-ray structure, magnetic study and DFT calculations

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Abstract

A new rare variety asymmetric μ_2-1,1-azido bridged copper(II) complex has been synthesized and characterized structurally and magnetically. The complex $[Cu_2L_2(\mu_2\text{-}1,1\text{-}N_3)_2] \cdot H_2O \cdot CH_3OH$ (L = 1-(*N-ortho*-hydroxyacetophenimine)-2-aminoethane) (**1**), crystallizes in monoclinic space group, $P2_1/n$, with $a = 9.469(4)$ Å, $b = 12.526(8)$ Å, $c = 12.899(10)$ Å, $\beta = 105.79(6)°$, $V = 1472.2(16)$ Å^3. X-ray study reveals that he Cu–N(azide)–Cu angles in this complex is 90.4°. This is unusually low in comparison to that of the same angle in other end-on azido-bridged binuclear complexes. Though a strong ferromagnetic interaction between the metal centers is expected in the complex, the coupling has actually been found to be antiferromagnetic ($J = -4.2$ cm^{-1}), instead. To rationalize this paradoxical magnetic behavior, DFT calculation of this and other four complexes with very similar structure have been performed within broken symmetry framework. The calculated magnetic coupling constants (J) are in excellent agreement, both in sign and in the magnitude of the exchange interaction, with the experimental data, and the spin density map is correctly reproduced.

Keywords: Copper(II)-azido complex; Dimer; DFT; Magnetic properties; X-ray crystal structure

1. Introduction

The design and magnetism of polynuclear complexes containing paramagnetic centers connected through pseudohalide bridges have attracted a lot of interest in recent times because of their importance in understanding the basics of magnetic interactions and magnetostructural correlations pertaining to the diverse fields encompassing condensed matter physics, materials chemistry, coordination chemistry, etc. [1]. Among pseudohalogens, azide received intense attention due to its versatility and efficiency in functioning as a bridging ligand to give varieties of coordination modes depending on the steric and electronic requirements of the other co-ligands present in the complex as well as its efficacy in extending suitable super-exchange pathways between several paramagnetic centers [2,3]. In fact, remarkable structural variations of azido complexes have resulted in a diversity of magnetic behavior. In a symmetric bi-bridged end-on azido dimers, the interaction is strongly ferromagnetic [4] while with one or more symmetric end-to-end azido bridges the interaction is strongly antiferromagnetic [5]. Complexes with asymmetric end-to-end azido bridge are usually weakly antiferromagnetic [4b], whereas complexes with asymmetric end-on azido bridges are rare, and showed a weak to moderately strong ferromagnetic interaction [6]. The studies concerning magneto-structural correlation including theoretical calculation of this type of complexes have been done by several groups of researchers [7–9a]. Various factors like strict and accidental orthogonality of magnetic

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orbitals [7,8], spin polarization [7], delocalization of unpaired electrons [7–9a] including charge transfer [1h,10] are found to have considerable influence in determining the characteristic of the magnetic coupling between paramagnetic centers. It has been shown that the magnetic interaction mediated by the azido bridge is generally antiferromagnetic for the $\mu_{1,3}$-N_3 (end-to-end, EE) mode, though in recent past some exceptions have been reported [11]. For the $\mu_{1,1}$-N_3 (end-on, EO) bridging mode, ferromagnetic ordering is established when the Cu–N–Cu angle is small which has been attributed to a spin polarization effect [12]. However, J_{ferro} is expected to decrease with increasing Cu–N–Cu angle, and the EO azido bridge can propagate antiferromagnetic coupling if the bridge angle is large enough (critical angle ~108°) [6,12,13]. More recent theoretical studies suggest a lower critical angle (~104°) [9a,14]. Other structural parameters like Cu–N(azido) distance, mean out-of-plane deviation of the azido group, geometry of the ligand environment to the Cu^{II} centers, ... shall also be considered [6,9a,13,14]. Therefore, end-on azido bridged polynuclear metal complexes certainly have relevance to the field of molecular magnetism. Interestingly μ-1,1-azido copper(II) dimers in which bridging azido ligand connects two metal centers through basal–apical coordination, magnetic interaction is sparsely found to be ferromagnetic though the Cu–N(azide)–Cu angle remains within the limit of lower critical value [15]. Recently, Ray et al. [1c] have considered H-bonding as the possible ferromagnetic interaction pathways in μ_2-1,1-azido copper(II) dimers containing similar kind of co-ligands. Theoretical calculations have rarely been undertaken to rationalize this paradoxical magnetic behavior of this type of complexes.

In an earlier attempt, we have succeeded in isolating rather a rare variety of asymmetric μ_2-1,1-azido copper(II) dimer using a tridentate Schiff base, 1-(*N*-salicylideneimino)-2-aminoethane as co-ligand [15]. This antiferromagnetic dimer shows an unusually low Cu–N(azide)–Cu angles. Further exploration of copper(II)-azido systems based on similar kind of co-ligands has allowed us to structurally and magnetically characterize a new antiferromagnetic Cu^{II}-azido system, $[Cu_2L_2(N_3)_2]\cdot H_2O\cdot CH_3OH$ (L = 1-(*N*-*ortho*-hydroxyacetophenimine)-2-aminoethane) having Cu–N(azide)–Cu angles equal to 90.1°. This led us to undertake full structure-based DFT calculations of the title complex and similar other μ_2-1,1-azido copper(II) dimers to rationalize their observed magnetic behavior.

As regards the theoretical calculations of magnetic exchange coupling constant (J) is concern Hoffmann's model [9b] offers a qualitative way to study the magnetic behavior of the binuclear complexes. However, this approach is not suited to predict the magnetic properties of new compounds. First principle methods, namely ab initio and DFT can give direct evaluation of the exchange magnetic coupling constant J. DFT is particularly suited for this purpose, since it can provide detailed information on the electronic structure and a good estimation of parameter J, in which we are interested. Within this framework, hybrid approach which combines Hartree–Fock-type and DFT-type contributions are often adapted for this type of calculations [14b,16,17]. The method we have followed in this work is the widely used B3LYP hybrid functional [18]. This method is not only found to be successful in describing the magnetic behavior of the complexes correctly but also yielded J that are in good agreement with the experimental values.

2. Experimental

2.1. Materials

Copper(II) nitrate trihydrate (Aldrich) and sodium azide (Sigma) were used without further purification. All other chemicals used were of AR grade.

2.2. Synthesis

Caution! Although our samples never exploded during handling, azide metal complexes are potentially explosive: only a small amount of material should be prepared and it should be handled with care.

2.2.1. Synthesis of $[Cu_2L_2(N_3)_2]\cdot H_2O\cdot CH_3OH$ (**1**)

To prepare the complex **1**, the methanolic solution of ethylenediamine (0.28 ml, 4.6 mmol) was added to a clear solution of $Cu(NO_3)_2\cdot 3H_2O$ (1 g, 4.14 mmol) dissolved in 25 ml methanol, which produced immediately an intense blue colored solution. The solution was then heated to boiling and a methanolic solution of *o*-hydroxy-acetophenone (0.44 ml, 3.6 mmol) was added dropwise slowly in 2 h in refluxing condition. After the completion of the addition of the *o*-hydroxy-acetophenone reflux was continued for another 45 min. On cooling the mixture a green slurry was obtained. The resulting green mass was then filtered out and an excess amount of sodium azide (1 g, 15.4 mmol) dissolved in a minimum volume of water was added to the filtrate. On slow evaporation of the resulting bluish-green colored solution the dark green block shaped single crystals of the complex were separated out in two days. The crystals were filtered and washed with methanol and dried in air. $[Cu_2L_2(N_3)_2]\cdot H_2O\cdot CH_3OH$ (**1**). Yield ca. 60%. *Anal.* Calc. for $C_{11}H_{19}N_5O_3Cu$: C, 39.7; H, 5.7; N, 20.9. Found: C, 39.5; H, 5.8; N, 21.1%. IR (KBr pellets, cm^{-1}): ν_{as}(azido) 2040 ; ν(C=N) 1640; ν(N–H) 3290.

2.3. Physical measurements

The facilities used for all physical measurements and the specific procedure used for fitting the magnetic data have been described earlier [1d].

2.4. X-ray crystallography

Intensity data of **1** were collected on a Bruker Nonius CAD4 diffractometer with graphite monochromated Mo

Kα radiation ($\lambda = 0.71073$ Å). A total of 2655 data were collected using the ω–2θ scan technique in the range to a maximum $4.62° < 2\theta < 50.0°$. Of the 2655 reflections, which were, collected 2540 were unique. The structure was solved by direct method [19] and refined by SHELX 97 [20]. Hydrogen atoms were included and also refined. Crystallographic data for complex **1** are summarized in Table 1.

2.5. Methodology of DFT calculations

The magnetic interaction between two paramagnetic centers with local spin operators $\vec{S}_1$ and $\vec{S}_2$ can be written in a spin Hamiltonian suggested originally by Heisenberg et al. [21–23]

$$H = -J\vec{S}_1.\vec{S}_2.$$

In this study, the broken symmetry (BS) formalism, proposed by Noodlemann et al. [24–26] is used. This approach is a useful tool that is accessible through the DFT framework and successfully applied in rationalizing magnetic behavior of several transition metal complexes earlier [4a,9a,14b,16,17,27–32]. For the present systems with two unpaired electrons on the magnetic centers (copper(II) with d^9 configuration), the coupling constant (J) or the singlet–triplet gap can be defined by

$$J = E_{BS} - E_T, \tag{1}$$

where E_{BS} is the energy of the broken symmetry state, Eq. (1) corresponds with non-spin-projected energy. The broken symmetry single determinant is the spin polarized solution of the Kohn–Sham equations for the singlet state using different spatial orbital for different spins [33].

Another expression of J as a function of BS and highest spin (HS) state energies can be obtained assuming only that the SOMO's are orthogonal. Noodlemann [34] referred to this approximation as the *weak bonding* regime and for our case, with one unpaired electron per magnetic center, we have

$$J = 2(E_{BS} - E_{HS}). \tag{2}$$

This means that the spin-orbitals of the magnetic centers are fully localized. This procedure does not account for reduced spin contamination in species with diminished diradical character. Correction based on spin projected method has been included [35,36], and the value of J has the following expression:

$$J = \frac{2(E_{BS} - E_{HS})}{\langle S^2\rangle_{HS} - \langle S^2\rangle_{BS}} \tag{3}$$

the value of $\langle S^2\rangle$ is calculated using the following formula [37] as implemented in the ADF program [38,39] (see next section)

$$\langle S^2\rangle = \langle S^2\rangle_{exact} + N^{\beta} - \sum_i^N \sum_j^N |S_{ij}^{\alpha\beta}|^2,$$

with

$$\langle S^2\rangle_{exact} = \left[\frac{N^{\alpha} - N^{\beta}}{2}\right]\left[\frac{N^{\alpha} - N^{\beta}}{2} + 1\right],$$

S_{ij} is the overlap integral of α-orbital i with β-orbital j, and N is the number of electrons where $N^{\alpha} \geqslant N^{\beta}$.

Table 1
Crystallographic data for complexes **1**

Empirical formula	$C_{11}H_{19}N_5O_3Cu$
Formula mass	332.85
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	9.469(4)
b (Å)	12.526(8)
c (Å)	12.899(10)
β (°)	105.79(6)
V (Å^3)	1472.2(16)
Z	4
$\rho_{calcd.}$ (gm cm^{-3})	1.502
μ (mm^{-1})	14.98
θ_{max} (°)	24.99
Crystal size (mm)	$0.50 \times 0.30 \times 0.20$
$F(000)$	692.00
Reflections measured	2655
Unique reflections	2540
$R1$	0.0903
$wR2$	0.2296

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(|F_o| - |F_c|)^2] / \sum [w(F_o^2)]^{1/2}$.

2.6. Computational details

The calculations were carried out using the Amsterdam Density Functional (ADF) package version (2004.01) [38,39]. All electron calculations using triple-ζ STO set plus one polarization function (TZP) were done. Both the Local Density Approximation (LDA) and the hybrid (Hyb-GGA) for exchange-correlation functionals were used. The LDA was applied with the Vosko et al. functional [40], the hybrid method was applied using the hybrid functional B3LYP, Becke for the exact exchange part and Lee–Yang–Par for the correlation part [18]. The implementation in ADF of the calculations of the exact exchange (Hartree–Fock exchange), which is needed for the hybrid method, is based on work published by Watson et al. [41].

The experimentally determined geometries for the complete structures of compounds **A**–**D** and complex **1** were used for the calculation of the magnetic exchange coupling constants. Neither variation of the geometrical parameters nor the geometry optimization [16] were attempted in this calculations because a small variation in the geometry can have a big effect on the calculated magnetic interaction parameters.

3. Results and discussion

3.1. X-ray structure of complex *1*

The structures of the complexes **1** with atom numbering scheme are given in Fig. 1. The selected bond distances and

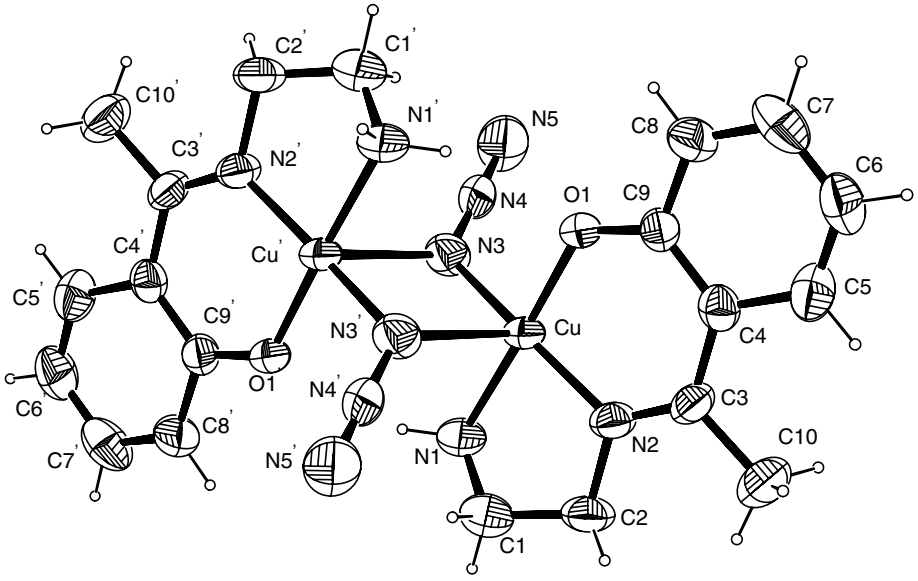

Fig. 1. ORTEP diagram of complex **1** showing atom numbering scheme. Solvent molecules are omitted for clarity.

angles of the complexes **1** are gathered in Table 2. The complex features a double μ-1,1-azido bridged copper(II) dimer. The copper(II) ion has a distorted penta-coordinated geometry in which the basal plane is composed of the three nitrogen donor atoms and one oxygen atom. Amongst them one nitrogen atom is from the bridging azide anion and the other two nitrogen atoms are from the tridentate Schiff base present in the complex. The remaining coordinate positions are occupied by the phenoxo oxygen of the tridentate Schiff bases. On the other hand, the fifth coordination site of the square pyramid in **1** is occupied by the nitrogen atom of the symmetry related azide group (symmetry: $-X+1$, $-Y$, $-Z$) forming the Cu–Cu bridge (Cu–Cu′ distance = 3.2636(24) Å). Therefore, in the present complex two metal ions are bridged by two azido ligands through basal–apical coordination linkage. The Cu–N3–Cu′ (or Cu′–N3′–Cu) angle is found to be ca. 90.4° in complex **1**. In the equatorial plane, the bond lengths of Cu–N3 (or Cu′–N3′) and Cu–N3′ (or Cu′–N3) are 1.990(9) and 2.569(9) Å, respectively. These inequalities in bond lengths give the both azido complexes a rare variety of asymmetric end-on double-bridged structures. The trigonality index τ ($=(\phi_1-\phi_2)/60$, where ϕ_1, ϕ_2 are the two largest L–M–L angles of the coordination sphere) [42] has been calculated for the two pentagonal copper sites. $\tau = 0.209$ and 0.206 for Cu1 and Cu3, respectively, confirming the square pyramidal character of both sites ($\tau = 0$ infers a perfect square pyramid, and a $\tau = 1$ a perfect trigonal bipyramid). The complex **1** contains one molecule of H_2O and CH_3OH each as solvent of crystallization.

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Cu–O(1)	1.880(7)
Cu–N(1)	1.988(9)
Cu–N(2)	1.954(9)
Cu–N(3)	1.991(10)
O(1)–C(9)	1.298(12)
N(1)–C(1)	1.449(17)
N(2)–C(3)	1.272(14)
N(2)–C(2)	1.486(14)
N(3)–N(4)	1.198(14)
N(4)–N(5)	1.133(15)
C(1)–C(2)	1.51(2)
O(1)–Cu–N(2)	93.8(4)
O(1)–Cu–N(1)	176.6(4)
N(2)–Cu–N(1)	86.8(4)
O(1)–Cu–N(3)	90.8(4)
N(2)–Cu–N(3)	168.9(4)
N(1)–Cu–N(3)	89.2(4)
Cu–O(1)–C(9)	125.6(7)
Cu–N(1)–C(1)	105.5(7)
N(3)–N(4)–N(5)	178.4(12)
N(1)–C(1)–C(2)	110.5(11)
O(1)–C(9)–C(4)	126.6(10)

3.2. Magnetic properties

The magnetic susceptibility of the complex has been measured in the temperature range 300–2 K (Fig. 2). The χ_M at room temperature, 2.72×10^{-3} cm^3 mol^{-1} is slightly larger than the spin-only value of 2.52×10^{-3} cm^3 mol^{-1} expected for two isolated copper(II) ions ($S = 1/2$) assuming $g = 2.00$. As the temperature is lowered, χ_M increases slowly up to ca. 60 K then sharply to 95.11×10^{-3} cm^3 mol^{-1} upon cooling to 3 K. Decrease in χ_M is observed then at 2 K. This is a characteristic magnetic behavior of an antiferromagnetically coupled dimer. To estimate the magnitude of the antiferromagnetic coupling the magnetic susceptibility data (300–2 K) were fitted to the modified Bleaney–Bowers equation for two interacting copper(II) ions ($S = 1/2$) with the Hamiltonian in the form $H = -J\widehat{S}_1.\widehat{S}_2$. The susceptibility equation for such a dimeric system can be written as follows [7a]:

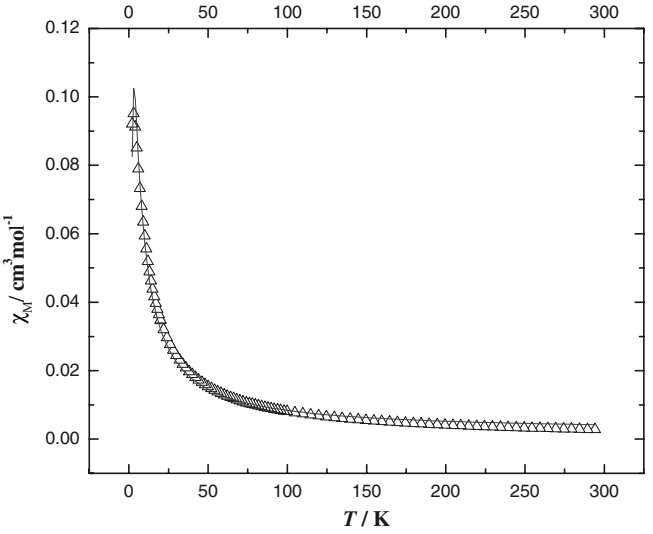

Fig. 2. χ_M vs. T (Δ) plot for complex **1**. Solid lines represent the best fit of the data with the model described in the text.

$$\chi = \frac{2Ng^2\beta^2}{kT}[3 + \exp(-J/kT)]^{-1}(1-\rho) + \frac{Ng^2\beta^2}{2kT}\rho, \qquad (4)$$

where N, g, β and ρ parameters in the equation bear their usual meaning.

The magnetic data fitting with the above equation affords the following parameters: $J = -4.2(2)\ \mathrm{cm}^{-1}$, $g = 2.10(1)$, $\rho = 0.003$ and $R = 4.6 \times 10^{-6}$ (disagreement factor). Though it is well established that end-on double azido bridged copper(II) dimers are usually ferromagnetic, our measurement indicates that the coupling between two copper(II) ions in this complex is clearly to be antiferromagnetic. This is really unusual for a dimer of this kind.

3.3. DFT calculations

To study the effect of the functional (LDA, GGA, etc.), we carried out in a first step DFT calculations with non-hybrid DFT functionals. The use of the GGA yields positive values (ferromagnetic interaction) of the calculated exchange magnetic coupling constants for the four complexes. Thus, the magnetic interaction is only well described for the compound **C**, which shows experimentally a ferromagnetic coupling ($J = 2.9\ \mathrm{cm}^{-1}$). The calculated J values for **C** using PW91 [43], BLYP [44–47], and BP [44,48] functionals (from Eq. (1)) are found to be 2.7, 2.55 and 3.01 cm^{-1}, respectively. For the present study, non-hybrid DFT functionals can describe correctly the ferromagnetic interaction for compound **C** only, but fails to reproduce experimentally observed magnetic interaction of the compounds showing antiferromagnetic coupling (**A**, **B**, **D**, and **1**). It is well established that the combination of Hartree–Fock (HF) and DFT within the B3LYP hybrid functional allows to get a good description for both broken-symmetry (BS) and high-spin (HS) states and hence yields the singlet–triplet gap (J) that are in good agreement with the experimental values [14b,16,17,27,49]. The results of the calculations for compounds **A**–**D** and **1** are given in Table 3. We have used three approaches via non-spin projected (Eq. (1)) and spin-projected methods (Eqs. (2) and (3)) to estimate the magnetic coupling constant of all the compounds. It is clear from the comparison of results obtained that the two spin-projected techniques give essentially the same results. This is due to the fact that the broken-symmetry (BS) and high-spin (HS) states are well localized, i.e., $\langle S^2\rangle_{BS} \simeq 1$ and $\langle S^2\rangle_{HS} \simeq 2$ in these cases. The results in the present study are in excellent agreement, both in sign and in magnitude of the exchange coupling constant, with experimental data. Spin-projected techniques, Eqs. (2) and (3), give most accurate results for compounds **B**, **D**, and **1**. On the other hand non-spin-projected, Eq. (1), gives a better agreement for complexes **A** and **C**. However, due to the strong localization of the wavefunction at the metal centers both computational technics produce results that are in remarkable agreement with the experimental value. In addition to the magnetic coupling constant, it is interesting to study the spin density distribution in the complexes. DFT calculations allow us to calculate Mulliken Spin Population in atoms/ions present in the coordination sphere of copper(II) including metal ion itself of the complexes **A**–**D** and **1** using B3LYP method. This type of calculations were successfully implemented in other $\mu_{1,1}$-azido copper(II) dimers earlier to understand the spin polarization mechanism and delocalization of the unpaired electrons of metal centers. Table 4 presents the calculated Mulliken spin densities for the triplet state using B3LYP hybrid method for the dimers **A**–**D** and **1**. Our result

Table 3
Comparison of calculated exchange coupling constants (cm^{-1}) (using spin-projected [Eqs. (2) or (3)] or non-spin projected [Eq. (1)] methods) and experimental results (Expt.)

Compounds	$\langle S^2\rangle_{BS}$	$\langle S^2\rangle_{HS}$	Eq. (2)	Eq. (3)	Eq. (1)	Expt.
A	1.0036	2.0035	−6.62	−6.62	−3.31	−1.8
B	1.0028	2.0030	−2.56	−2.56	−1.28	−3.1
C	1.0045	2.0043	8.34	8.34	4.17	2.9
D	1.0040	2.0039	−9.08	−9.08	−4.54	−8.5
1	1.0035	2.0036	−6.72	−6.72	−3.36	−4.2

Expectation values of total square spin operators for both broken symmetry (BS) and high spin (HS) states, used for Eq. (3), are shown.
All the compounds have same core structure, $[Cu_2L_2(\mu_{1,1}\text{-}N_3)_2]$. LH_2 for **A** is *N*-(3-aminopropyl)-salicylaldimine, for **B** is 7-amino-4-methyl-5-azahept-3-en-2-one, for **C** is 8-amino-4-methyl-5-azaoct-3-en-2-one and for **D** is 1-(*N*-salicylideneiimino)-2-aminoethane.

Table 4
Calculated Mulliken spin populations in the triplet state of the complexes (**A**–**D** and **1**) using B3LYP

	A	**B**	**C**	**D**	**1**
Cu	+0.52	+0.53	+0.52	+0.52	+0.52
N3	+0.076	+0.069	+0.081	+0.074	+0.08
N4	−0.008	−0.005	−0.009	−0.001	−0.007
N5	+0.098	+0.081	+0.11	+0.11	+0.1
N1	+0.098	+0.01	+0.09	+0.09	+0.08
N2	+0.1	+0.1	+0.08	+0.09	+0.09
O1	+0.11	+0.12	+0.13	+0.13	+0.13

convincingly demonstrates that there is an extensive delocalization of the unpaired electron on Cu(II). Small positive values of spin density on the bridging and terminal nitrogen atoms (N3 and N5) of the azido groups as well as on the other coordinated atoms (N1, N2 and O1), and weakly negative on the central nitrogen atoms (N4) of the N_3^- bridge were observed in the present calculations. This is in agreement with the other reports available in the literature [9a,14a]. The sign alternation of the spin density at the N4 and N5 atoms of the azido-bridge is consistent with spin polarization by the bridging nitrogen atoms.

Full molecule calculation using hybrid B3LYP functional to reproduce singlet–triplet energy gap of μ_2-1,1-azido copper(II) complexes is not only found to be successful in describing the magnetic behavior of the complexes correctly in this study but also yielded *J* that are in excellent agreement with the experimental value. Pure DFT functional fails to afford satisfactory analysis of magnetic behavior of these complexes. The magneto-structural correlations including DFT calculation derived results of μ_2-1,1-azido copper(II) complexes which have metal–metal azido bridge through basal–basal coordination linkage could not be applied as such to the complexes those are possessing basal-apical linkage to explain experimentally observed magnetic data of the latter class of complexes. Nonetheless full molecule DFT based calculation based on X-ray structural data could be successfully used to rationalize the magnetic behavior of this class of complexes.

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Appendix A. Supplementary data

Further details of structure determination including tables of atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles for the complex 1. Supplementary data are available from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) on request, quoting the deposition number CCDC 279465. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.09.005.

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